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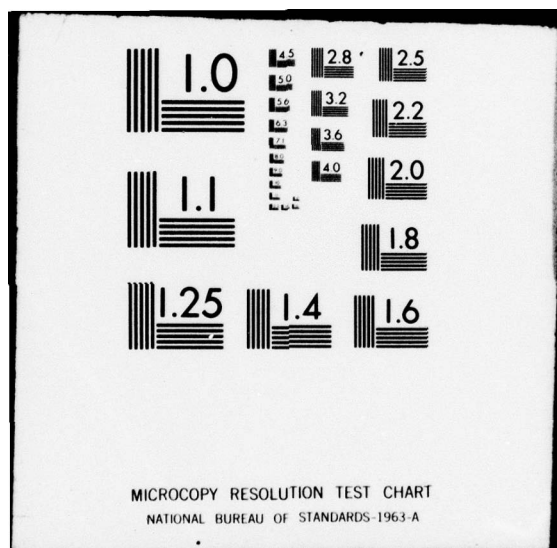
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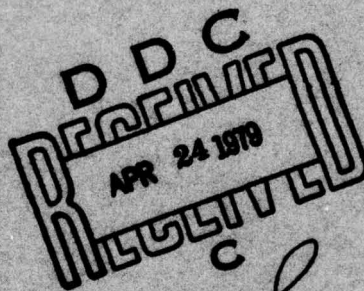
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FRANK J. SEILER RESEARCH LABORATORY

FJSRL TECHNICAL REPORT-78-0014

DECEMBER 1978

MEASUREMENT OF TRANSPORT PROPERTIES OF
SEVERAL N-ALKYLPYRIDINIUM HALIDES
AND THEIR MIXTURES WITH
ALUMINUM CHLORIDE



RONALD A. CARPIO
LOWELL A. KING
RICHARD E. LINDSTROM
JOHN C. NARDI
CHARLES L. HUSSEY

PROJECT 2303

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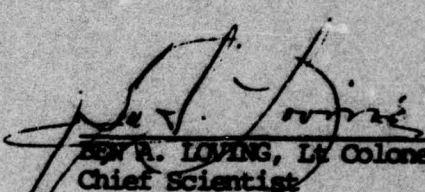
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This technical report has been reviewed and is approved for publication.


RONALD A. CARPIO, Captain, USAF
Project Scientist


KENNETH E. SIEGENTHALER, Lt Colonel, USAF
Director
Directorate of Chemical Sciences

FOR THE COMMANDER


LEW A. LOVING, Lt Colonel, USAF
Chief Scientist

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Densities and viscosities were measured and equivalent conductivities calculated for each of the 1:2 melts.

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MEASUREMENT OF TRANSPORT PROPERTIES
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By

Ronald A. Carpio, Lowell A. King
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INTRODUCTION

This report summarizes our transport parameter measurements, conducted over a wide temperature range, on several N-alkylpyridinium halide salts (RPX) and their 1:2 RPX- AlCl_3 eutectic mixtures. We determined the specific conductivities of molten N-methyl-, N-ethyl-, N-(n-propyl)- and N-(n-butyl)-pyridinium chlorides and N-ethylpyridinium bromide from near the melting points to the thermal decomposition temperatures. Conductivities also were measured from 25 to 125° C for each of the 1:2 RPX- AlCl_3 mixtures and from 97 to 127° C for 1:1 N-ethylpyridinium chloride- AlCl_3 .

Densities and viscosities were measured for each of the 1:2 melts from 25 to 75° C.

EXPERIMENTAL

Sample Preparation. - The preparation of N-alkylpyridinium salts and their binary mixtures with AlCl_3 is described elsewhere (1).

Density Measurements. - Densities were measured in sealed Pyrex dilatometers whose volumes had been calibrated with mercury or distilled H_2O in the conventional manner. Meniscus readings were related to a mark on the capillary stem, as has been described previously (2). The volume of the dilatometer to this reference mark was typically 4.5 cm^3 and that of the capillary bore was typically $1.8 \times 10^{-3} \text{ cm}^3/\text{mm}$. Each dilatometer was loaded with the liquid sample in a nitrogen-filled glove box. (Vacuum/Atmospheres Co., Model HE-53-6 DRI LAB - moisture content less than 2 ppm) using a syringe attached to a long needle to avoid gas entrapment. The dilatometer was then stoppered, removed from the dry box, evacuated, and sealed with a torch. Cathetometer readings were made to an accuracy of $\pm 0.05 \text{ mm}$. Corrections for buoyancy, thermal expansion, and meniscus shape effects were insignificant and were omitted. An accuracy of $\pm 0.05\%$ was estimated.

Viscosity Measurements. - A closed capillary, suspended level, all glass viscometer, similar in design to that described by van Os and Ketelaar (3) was employed. The capillary diameter was such that flow times ranged between 140 and 450 sec. The viscometer was calibrated at 25°C using aqueous solutions of glycerol for which accurate viscosity data could be found in the literature (4) and having the same range of flow times as those of the samples studied. The calibration was required for the determination of the constants A and B in the equation

$$\nu = \frac{\eta}{\rho} = A\theta - \frac{B}{\theta} \quad [1]$$

where ν is the kinematic viscosity, η is the dynamic viscosity, ρ is the density, and θ is the efflux time. Efflux times were measured with a stopwatch with a precision of better than $\pm 1.5\%$. Combining this error with those in temperature, density, composition, and that due to misalignment of the capillary from the vertical (5), an overall error of $\pm 2.5\%$ in the dynamic viscosity was estimated. The greatest error was associated with temperature uncertainty. The viscometer possessed a narrow neck above the main bulb which was essential for measurement accuracy but which led to difficulties in recharging the bulb with liquid. In order to prevent the formation of air locks during the recharging operation, the viscometer had to be removed from the bath momentarily and tapped. The measurements were not extended above 75°C for this reason. At least 3 runs were made at each temperature and the mean efflux times were computed.

Conductivity Measurements. - U-shaped Pyrex conductance cells with the two arms connected by a capillary tube similar to that described by Moynihan (6) were found to be quite satisfactory for these studies, since these liquids have low vapor pressures. The electrodes were bright platinum plates of 0.5 and 1.0 cm^2 area. The electrodes were spot welded to platinum wires which were in turn sealed in Pyrex tubes according to the procedure described by Evans and Matesich (7). These glass tubes at their upper ends were connected to the cell arms by means of ball-and-socket joints. The cell utilized for the pure melts was calibrated at 25°C using a 1 demal aqueous KCl solution; that used for the binary mixtures was calibrated

using 0.1 normal aqueous KCl solution, as recommended by Janz and Tomkins (8). The cell constants were 552.39 cm^{-1} and 71.92 cm^{-1} , respectively.

The majority of the conductivity measurements were made at 1 kHz and 3 kHz with a Beckman Model RC-18A conductivity bridge. This bridge is essentially a Wheatstone bridge coupled with a phase sensitive CRT null detector, a Wagner ground circuit, and a sharply tuned amplifier. The conductivity of the pure salts varied by $\pm 0.05\%$ or less between 1 and 3 kHz. Thus, no frequency corrections were considered necessary. However, the conductivity for the binary mixtures varied by as much as $\pm 0.5\%$ over this same frequency range. Consequently, it became necessary to measure the frequency dispersion of the conductance with a General Radio 1608-A impedance bridge, coupled with a 1161-A General Radio frequency synthesizer which supplied a sine wave of accurately defined frequency, and a Hewlett Packard 132 dual beam oscilloscope detector to establish a phase balance. The amplitude of the applied sine wave was minimized in order to prevent Faradaic processes from occurring and, as a result, it was found necessary to condition the low amplitude output signal from the impedance bridge with a differential amplifier and a Krohn-Hite Model 3103 adjustable bandpass filter before it was fed into the oscilloscope. The resistance of the binary mixtures depended linearly upon the square root of frequency over the range 0.5 to 15 kHz. Consequently, this functional form was employed to extrapolate the resistance to infinite frequency. The computed polarization-free resistance at infinite frequency was employed to calculate the specific conductivity.

The conductivity cells were loaded in the nitrogen-filled glove box. Care was exercised in the case of the ambient temperature melts to prevent bubble entrapment in the capillary. In the case of the pure pyridinium salts, the conductivity cell was placed in a furnace and maintained slightly above the melting point of the salt. The salt was then added until a sufficient volume of melt was obtained, then the electrodes were positioned in the cell.

Conductances were measured at temperature intervals of approximately 5°C over both ascending and descending temperature ranges. Measurements on the pure pyridinium salts were begun just above the melting point and terminated when decomposition commenced, which could be easily detected by the appearance of bubbles within the liquid. Excellent reproducibility of different samples was attained. Such was also the case when comparisons were made between different batches of the binary mixtures which had been subjected to varying degrees of purification by electrolysis.

Errors in Conductivity. - At most a 0.2% error resulted from equating the bridge reading R_p to the solution resistance R_s . In the case of the Beckman RC-18 conductivity bridge, the balancing impedance consisted of a variable resistance, R_p , and capacitance, C_p , connected in parallel. Thus, since the equivalent circuit representation for a conductance cell is a series combination of the solution resistance R_s and solution-electrode interfacial capacitance, C_s , it can be shown (9) that

$$R_s = R_p / [1 + R_p^2 C_p^2 (2\pi f)^2]$$

where f is the ac frequency. A second cause of error was the accuracy with which the resistance R_p could be measured, which was $\pm 0.05\%$. The temperature

uncertainly, $\pm 0.03^{\circ}\text{C}$, translated roughly into less than 0.1% error. A calibration error of 0.1% was also another source of error. Lastly, impurities in the pyridinium salts probably contributed less than 0.5% error to conductance values.

Temperature Control and Measurement. - A water bath, contained in a large, rectangular, Pyrex battery jar, and a Fisher Isotemp bath controller were employed for the viscosity and density measurements. Temperature stability of at least $\pm 0.03^{\circ}\text{C}$ was attained over the temperature range 25°C to 75°C .

The conductivity measurements were made in a Haake constant temperature bath over the temperature range 25°C to 50°C . Measurements at higher temperatures were conducted in a stirred silicone oil bath for which temperature was controlled to better than $\pm 0.03^{\circ}\text{C}$ with a Bayley Model 124 proportional temperature controller.

Temperature monitoring was accomplished with an Air Force Standard Platinum Resistance Thermometer, which had been calibrated at the freezing point of zinc, freezing point of tin, boiling point of water, triple point of water, and the boiling point of oxygen by the U.S. Air Force Measurement Standards Laboratory, Aerospace Guidance and Metrology Center, Newark Air Force Station, Ohio.

RESULTS AND DISCUSSION

The specific conductivity measurements are given in Table I. The data were fit to the polynomial

$$\kappa = a_0 + a_1 t + a_2 t^2 \quad [2]$$

where κ is the specific conductivity in $\Omega^{-1} \text{cm}^{-1}$, a_0 , a_1 , and a_2 are parameters, and t is the temperature in $^{\circ}\text{C}$. The computer fitted parameters are given in Table II.

Densities and viscosities of the ambient temperature melts are given in Table III. Densities were fit to the polynomial

$$\rho = a_3 + a_4 t \quad [3]$$

where ρ is the density and a_3 and a_4 are parameters. The computer fitted parameters are given in Table IV. The dynamic viscosities, η , in Table III of the room temperature melts were evaluated using Eq. [1] and the measured densities.

The viscosities displayed an Arrhenius temperature dependence over the approximate temperature range 25 to 75°C ; i.e.,

$$\eta = \eta_0 \exp(E_{\eta}/RT) \quad [4]$$

where E_{η} is the energy of activation for viscous flow, R is the gas constant, T is the temperature in kelvin, and η_0 is a parameter. Equation [4] was cast into the different form

$$\ln \eta = A_{\eta} + B_{\eta}/T \quad [5]$$

where $A_{\eta} = \ln \eta_0$ and $B_{\eta} = E_{\eta}/R$. The viscosities were fit to Eq. [5], and the computer fitted parameters are given in Table V.

These results, further calculations, and the significance of the work are presented in a companion publication (1).

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Table I. Specific conductivities.

$t, ^\circ\text{C}$	$\kappa, \text{ohm}^{-1}\text{cm}^{-1}$	$t, ^\circ\text{C}$	$\kappa, \text{ohm}^{-1}\text{cm}^{-1}$
MPC		1:1 EPC-AlCl ₃	
149.21	0.08875	97.18	0.05392
149.79	0.08938	104.74	0.05915
155.54	0.09804	111.88	0.06424
156.76	0.09778	119.11	0.06957
159.89	0.10485	126.69	0.07522
169.18	0.11965		
179.87	0.13750	1:2 MPC-AlCl ₃	
184.70	0.14527	25.17	0.00827
189.07	0.15312	34.40	0.01076
194.62	0.16266	53.84	0.01694
		61.76	0.01986
EPC		67.25	0.02201
124.67	0.05269	74.23	0.02485
129.74	0.05749	84.40	0.02972
138.04	0.06914	100.05	0.03649
145.14	0.07858	115.19	0.04418
149.61	0.08461	124.87	0.04927
155.70	0.09334		
PPC		1:2 EPC-AlCl ₃	
115.32	0.02097	25.17	0.01022
120.18	0.02431	30.53	0.01176
125.07	0.02789	34.89	0.01309
130.42	0.03207	40.64	0.01493
135.66	0.03625	46.34	0.01686
		56.96	0.02076
BPC		57.30	0.02098
139.63	0.02286	66.55	0.02462
149.82	0.02763	68.59	0.02555
		77.21	0.02912
EPB		78.06	0.02963
124.75	0.04467	85.83	0.03317
129.85	0.04971	96.77	0.03837
135.02	0.05504	106.24	0.04311
139.01	0.05930	114.81	0.04749
149.36	0.07086	124.62	0.05386
149.44	0.07083		
154.69	0.07702		
159.14	0.08260		
164.86	0.09002		

Table I. (Con't)

$t, ^\circ\text{C}$	$\kappa, \text{ohm}^{-1}\text{cm}^{-1}$	$t, ^\circ\text{C}$	$\kappa, \text{ohm}^{-1}\text{cm}^{-1}$
1:2 PPC-AlCl ₃		1:2 EPB-AlCl ₃	
25.17	0.00820	25.22	0.00851
31.04	0.00967	27.39	0.00901
35.27	0.01082	32.88	0.01049
39.78	0.01209	35.89	0.01132
42.59	0.01289	40.65	0.01270
49.76	0.01513	45.09	0.01404
50.74	0.01540	49.30	0.01540
54.65	0.01668	55.82	0.01756
61.30	0.01894	58.86	0.01865
67.36	0.02113	67.58	0.02184
67.52	0.02115	73.52	0.02413
86.58	0.02858		
104.59	0.03620		
124.76	0.04531		
1:2 BPC-AlCl ₃			
24.94	0.00687		
27.24	0.00723		
31.22	0.00825		
36.86	0.00960		
45.03	0.01170		
53.04	0.01395		
58.30	0.01538		
65.11	0.01750		
71.17	0.01952		
78.11	0.02187		
84.80	0.02428		
92.95	0.02725		
99.41	0.02965		
108.08	0.03300		
115.82	0.03619		
124.13	0.03976		
132.97	0.04354		

Table II. Parameters for specific conductivity equations (Eq. [2]).

<u>Melt</u>	<u>$a_0 \times 10^2$</u>	<u>$a_1 \times 10^3$</u>	<u>$a_2 \times 10^5$</u>	<u>$(\sigma \times 10^4)^*$</u>	<u>Temp. range, °C</u>
MPC	-5.6530	0.45349	0.34632	8.0	149-195
EPC	-2.3925	0.05826	0.44622	0.47	125-156
PPC	-0.6869	-0.1936	0.3771	0.41	115-136
BPC	-4.2373	0.4672	—	—	140-150
EPB	-0.6579	-0.1301	0.43401	0.92	125-165
1:1 EPC-AlCl ₃	-0.04928	0.43512	0.12834	0.25	97-127
1:2 MPC-AlCl ₃	0.21631	0.20160	0.14143	2.1	25-125
1:2 EPC-AlCl ₃	0.3944	0.21033	0.15034	1.7	25-125
1:2 PPC-AlCl ₃	0.2230	0.2028	0.1151	1.0	25-125
1:2 BPC-AlCl ₃	0.1686	0.1763	0.1048	0.87	25-133
1:2 EPB-AlCl ₃	0.3164	0.17209	0.15402	0.17	25-74

* σ in this and subsequent tables is the RMS deviation in the dependent variable as calculated at each experimental point from the least-squares curve.

Table III. Densities and viscosities of 1:2 N-alkylpyridinium- AlCl_3 mixtures.

<u>t, °C</u>	<u>ρ, g cm⁻³</u>	<u>η, cP</u>	<u>t, °C</u>	<u>ρ, g cm⁻³</u>	<u>η, cP</u>
1:2 MPC- AlCl_3			1:2 EPB- AlCl_3		
25.17	1.4402	20.781	24.99	1.5241	22.494
36.19	1.4317	15.647	32.05	1.5175	17.724
47.10	1.4213	11.738	44.21	1.5062 ^a	12.834 ^b
62.99	1.4076	8.438	51.73	1.4992 ^a	10.859 ^b
74.99	1.3972	6.834	59.27	1.4922 ^a	9.114 ^b
1:2 EPC- AlCl_3					
25.17	1.4079	17.786			
39.34	1.3946	12.104			
52.76	1.3824	9.611			
67.44	1.3692	7.069			
78.70	1.3588 ^a	5.863 ^b			
1:2 PPC- AlCl_3					
25.65	1.3748	18.143			
31.04	1.3699	15.778			
42.59	1.3595	11.597			
50.74	1.3523	9.609			
61.30	1.3430	7.952			
67.52	1.3376	7.138			
74.69	1.3314	6.139			
1:2 BPC- AlCl_3					
30.88	1.3417	18.081			
40.31	1.3330	13.823			
53.43	1.3220	10.020			
60.85	1.3157	8.347			
66.98	1.3104	7.422			
76.07	1.3026	6.319			

^a Extrapolated value using Eq. [3].

^b Calculated using extrapolated ρ .

Table IV. Parameters for density equations (Eq. [3]).

<u>Melt</u>	<u>\underline{a}_3</u>	<u>$-\underline{a}_4 \times 10^3$</u>	<u>$\sigma \times 10^4$</u>	<u>Temp. range, °C</u>
1:2 MPC-AlCl ₃	1.4625	0.87103	4.8	25-75
1:2 EPC-AlCl ₃	1.4307	0.91446	1.7	25-67
1:2 PPC-AlCl ₃	1.3973	0.8847	1.4	26-75
1:2 BPC-AlCl ₃	1.3680	0.86042	2.1	31-76
1:2 EPB-AlCl ₃	1.5473	0.93059	—	25-32

Table V. Parameters for Arrhenius equations for viscosity (Eq. [5]).

<u>Melt</u>	<u>$\frac{-A}{\eta}$</u>	<u>$\frac{B}{\eta} \times 10^{-4}$</u>	<u>$\frac{E}{\eta}$, kcal mol⁻¹</u>	<u>$\sigma \times 10^2$</u>
1:2 MPC-AlCl ₃	4.801	0.2334	4.639	2.0
1:2 EPC-AlCl ₃	4.355	0.2152	4.276	2.7
1:2 PPC-AlCl ₃	4.734	0.2276	4.523	2.1
1:2 BPC-AlCl ₃	5.314	0.2491	4.950	1.9
1:2 EPB-AlCl ₃	5.575	0.2584	5.136	1.9